Defense Technical Information Center
Compilation Part Notice

ADP013618

TITLE: Chemical Sensing With Resistive Microcantilevers

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Materials Research Society Symposium Proceedings. Volume 723.
Molecularly Imprinted Materials - Sensors and Other Devices. Symposia
Held in San Francisco, California on April 2-5, 2002

To order the complete compilation report, use: ADA412559

The component part is provided here to allow users access to individually authored sections
of proceedings, annals, symposia, etc. However, the component should be considered within
the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:
ADP013597 thru ADP013618

O6.8

Chemical Sensing With Resistive Microcantilevers

G. Muralidharan[1], A. Wig[1], L. A. Pinnaduwage[1], D. L. Hedden[1], P. G. Datskos[1], T. Thundat[1], and R. T. Lareau[2]
[1]Oak Ridge National Laboratory, Oak Ridge, TN-37831-6123.
[2]Federal Aviation Administration, Atlantic City, NJ 08405.

ABSTRACT

MEMS-based microcantilevers have been proposed for a variety of biological and chemical sensing applications. Measuring the magnitude of microcantilever deflection due to adsorption-induced bending, and following the variation in the resonant frequency of the microcantilevers due to the adsorbed mass are two techniques commonly employed for sensing analytes. Apart from possessing a high level of sensitivity to small changes in mass, microcantilevers are also very sensitive to small changes in temperature and hence the flow of heat. One way of achieving high sensitivity in thermal measurements is by using a bimaterial microcantilever and measuring its deflection as a result of thermal fluctuations. Commercially available piezoresistive microcantilevers are an example of bimaterial cantilevers and in this study, we propose the use of such cantilevers for sensing explosives. We show that sensing can be accomplished by following the differences in the thermal response of the cantilevers introduced by the presence of explosives adsorbed from the vapor phase onto the surface of the cantilever. We discuss the issues involved in determining the sensitivity of detection and selectivity of detection.

INTRODUCTION

Real-time detection of explosives is important for practical applications ranging from passenger baggage-screening to the disarming of landmines. With their compactness and potential low cost, detection techniques based on Silicon-based Micro Electro-Mechanical Systems (MEMS) provide a path for the development of miniaturized sensors. One method for detecting explosives is through the detection of vapors in equilibrium with the solid explosive [1]. To design devices that would detect explosive chemicals such as TNT through detecting the presence of their vapors, a detailed understanding of the physical chemistry parameters involved in vapor transport, knowledge of the diffusion coefficients, molecular sticking coefficients and vapor pressures over non-ideal solid solutions are all of importance[2]. In addition, detailed knowledge of the interaction of such explosive vapors with exposed surfaces is of interest. For example, it would be of interest to know how much vapor would adsorb and stick to the sensing surface over a certain period of time under typical conditions at which the sensor would be used. Although data are available on the long-term adsorption and desorption of vapors such as TNT from surfaces of soils [3], very little data is available on the short-term behavior related to surfaces that would be common in MEMS. This information along with the known minimum detectable quantity would determine the time necessary for detection. In addition, knowledge of the relative affinities of different surfaces to these vapors would help in designing surfaces that would maximize sensitivity while minimizing detection time.

One characteristic of explosives that make detection of vapors difficult is their very low equilibrium vapor pressures at room temperature. For example, it is very well known that for TNT, this is in the range of ppb$_v$ at room temperature. Under conditions where dilution is possible, such as in an open atmosphere, it is expected that the vapor pressures will be in the of ppt$_v$ range [2]. Hence the technique used to measure the adsorption of TNT onto surfaces has to be sensitive to measure small changes in the amount of adsorbed analyte. Various studies in the past have shown that MEMS-based microcantilevers can be used for a wide range of chemical and biological sensing applications with very high level of sensitivites [4-8]. It has been demonstrated that sensing using cantilevers can be established either through the measurement of changes in its resonant frequency or through the measurement of bending induced by changes in surface stress. Resonant frequency changes are caused by the adsorption of the analyte onto the surfaces of the cantilever with a resultant change in the overall mass. On the other hand, bending is induced in the cantilever when the two surfaces of the cantilever have different affinities for the analyte which results in differential adsorption. Prior studies shown that pg-level mass resolution can be achieved when cantilevers are used for sensing changes in mass using the changes in the resonant frequency of the cantilever [8]. Selectivity in these experiments is achieved by coating one of the two surfaces of the cantilever with a chemical that interacts preferentially with the analyte of interest. Chemicals, self-assembled monolayers, and polymers have been used in previous studies to achieve selectivity [7,9].

In the current study, we present a method that uses uncoated piezoresistive cantilevers as the sensing element. We follow the adsorption and desorption of TNT from a Si/SiO$_2$-surface exposed to the vapors using the variation in the resonant frequency of the cantilever. During adsorption, the resonant frequency of the cantilever decreases due to an increase in mass while the resonant frequency of the cantilever increases during desorption since the total mass associated with the cantilever decreases. After the desired amount of TNT has been adsorbed onto the surface of the cantilever, the microcantilever is rapidly heated to induce reactions on its surface due to the presence of TNT. We show that the response of the piezoresistive cantilever to an applied voltage varies with the amount of TNT adsorbed on its surfaces. We discuss how this methodology can be used to selectively detect TNT. This technique is versatile since such studies are conducted with "real-surfaces" and at ambient conditions.

EXPERIMENTAL METHOD

Figure 1 shows a schematic of the experimental setup. The setup used for the measurements was designed to follow the time-dependent behavior of the microcantilever using light reflected from the surface of the cantilever. A red solid-state laser was used as the light source while a two-quadrant Position Sensitive Detector (PSD) converts the reflected light signal into a voltage that is proportional to the position of the light incident on the detector. Commercially available piezoresistive microcantilevers were used for these experiments since the piezoresistive layer can be used as a heating element to rapidly heat the cantilever. Figure 2 shows a Scanning Electron Microscope image of the commercially available microcantilevers.

To follow the changes in resonant frequency, the piezoresistive microcantilevers were driven using a speaker in the "feedback" mode. It has been shown previously that this method of
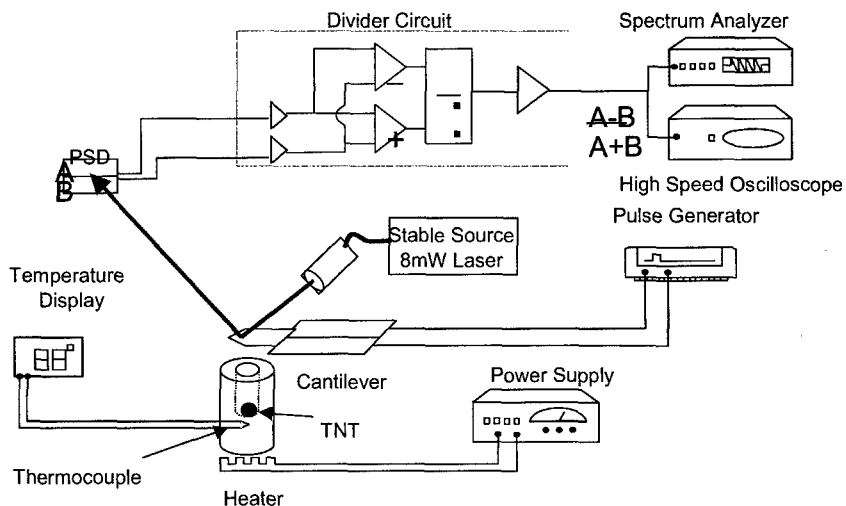
Figure 1. Schematic Showing Key Components of the Experimental Setup

excitation results in high-Q factors and hence better accuracy in real-time, fast data collection [10]. In contrast to the case where the cantilever is driven using an external signal generator source, this method is quicker since the cantilever is "self-tuning" and no external tuning of drive frequency is necessary. The frequency response of the microcantilever was measured using a high-speed digitizer /spectrum analyzer. The source of TNT vapor is a solid piece of TNT positioned at a distance of about 2-3 cm directly beneath the bottom surface of the microcantilever. The vapor pressure of TNT near the cantilever is varied by changing the temperature of the solid piece of TNT placed in the oven. A shutter is used to control the start and end of exposure. After the desired amount of TNT is adsorbed on the cantilever (as indicated by the change in resonant frequencies), a single square voltage pulse of magnitude 10 Volts is applied across the cantilever and the response of the microcantilever to this voltage pulse is followed as a function of time.

05KU   313X   31.9M 0105

Figure 2. SEM Image of a Typical Piezoresistive Micro cantilever used for the Experiments.

RESULTS AND DISCUSSION

Figure 3 shows the variation in resonant frequency of the microcantilever as a function of time when its surface was exposed to TNT vapors by opening the shutter. Before exposure to the TNT vapor, the surface was cleaned by resistively heating the microcantilever. The temperature of the oven

containing the solid TNT was maintained at 66°C while the cantilever was maintained at room temperature. This temperature of TNT was selected to enable adsorption of TNT onto the surface of the cantilever over a reasonably short period of time. However, the technique can also be used to monitor the adsorption of TNT at lower partial vapor pressures as would be observed when the TNT is maintained at lower temperatures. Note that the frequency decreases as a function of time and that the frequency changes fairly rapidly over a period of 15 minutes. This reduction in frequency can be attributed to an increase in the total cantilever mass, showing clearly that TNT adsorbs and sticks to the cantilever surface. From a knowledge of the mass of the microcantilever, the frequency change can be correlated to a change in mass using the expression

$$\left(\frac{f_0^2}{f_1^2} - 1 \right) m_0 = \delta m , \qquad (1)$$

where f_0 denotes the resonant frequency before adsorption of TNT, f_1 denotes the resonant frequency of the microcantilever after adsorption of TNT, m_0 the initial mass of the microcantilever, and δm is the change in mass of the cantilever. The increase in mass attributable to the adsorption of TNT is calculated using equation (1) and an initial cantilever mass of 130 ng and is shown on the right axes of the figures.

Figure 4 shows the variation in frequency after closing the shutter thus shutting off the source of TNT vapor. Note that the frequency increases gradually and returns to its original frequency over a period of over six hours indicating that the TNT that had adsorbed previously, desorbs from the surface of the microcantilever. It is important to note that desorption does occur under ambient conditions. Also to be observed are the relative values of the time-scales for adsorption and desorption. Note that under typical ambient conditions, it takes a relatively long period of time (many hours) to desorb the few nanograms of adsorbed TNT.

Figure 5 shows the response (voltage output from the PSD) of the cantilever as a function of time to an applied constant voltage pulse along with the effect of adsorbed TNT on the cantilever response. It should be noted that the settling time of the applied voltage is of the order of a few microseconds while the microcantilever response time to reach maximum deflection (for this particular cantilever) is of the order of 1 millisecond. Thus, thermal equilibrium between the microcantilever and its surroundings and not the rate of application of the voltage affects the
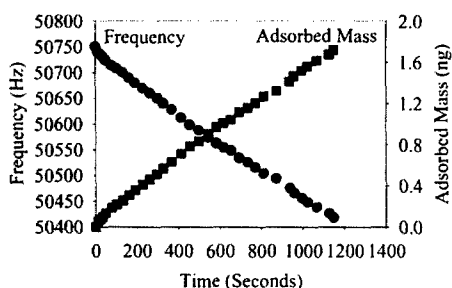

Figure 3. Variations in Cantilever Resonant Frequency and Adsorbed Mass as a Function of Time During Exposure to TNT Vapors.
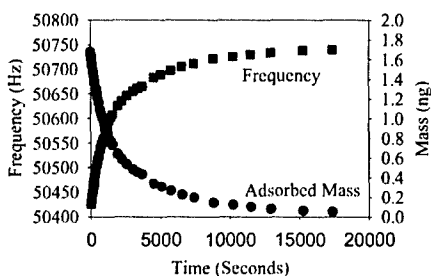
Figure 4. Variations in Cantilever Resonant Frequency and Adsorbed Mass as a Function of Time After the Removal of TNT Vapors.

rate of temperature rise within the cantilever. The variation in output voltage as a function of time shown in the figure can be understood based upon the structure of the microcantilever [11]. It should be noted that the microcantilever consists of a p-type Si-substrate and a p+-Si resistive layer protected by a thin oxide layer. As current passes through the conductive layers in the cantilever, the temperature of the microcantilever rises, and the microcantilever bends due to differential thermal expansion coefficients of the materials comprising the microcantilever (bimaterial effect). Since the coefficient of thermal expansion of Si (2.6×10^{-6} /K) is much larger than that of SiO_2 (4×10^{-7} /K), for a temperature rise ΔT, the microcantilever will bend towards the SiO_2 side (downwards in this geometry) thus resulting in a negative voltage output from the PSD as is verified experimentally from the figure.

Also evident from figure 5 is the effect of TNT in modifying the response of the cantilever. Note the presence of inflections in the curve even with small amounts of adsorbed TNT, with the inflections becoming enlarged to a clear maximum (a bump) with increasing amounts of TNT. This is illustrated clearly in figure 6, which shows the difference between the response of the microcantilever with and without adsorbed TNT for three different quantities of adsorbed TNT. Calculations show that the area under the difference curve is proportional to the amount of TNT adsorbed onto the surface of the cantilever. Thus, the effect of the presence of TNT is clearly manifested in the response of the cantilever to the heating pulse.

In summary, we have shown that explosive vapors such as TNT can be adsorbed onto microcantilever surfaces and detected through their influence on the bending behavior during rapid heating of these microcantilevers. Important factors to be considered in using this technique for detecting TNT are sensitivity and selectivity. Ability to detect about 70 picograms of TNT present on the cantilever has already been demonstrated while improvement in this value can be achieved by modifying the design of the cantilever. It has been observed that a minimum applied voltage (and hence cantilever temperature) is necessary to observe the responses shown in figure 5. This provides an avenue for obtaining selectivity in the detection of TNT vapors.
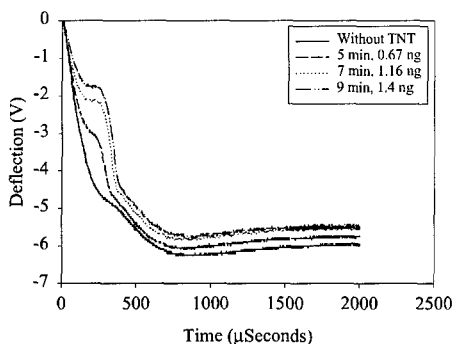

Figure 5. Effects of Varying Amounts of TNT on Cantilever Response to the Applied Voltage.
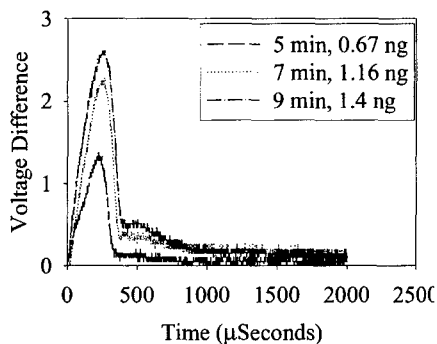
Figure 6. Differences Between the Responses of the Cantilever to the Applied Voltage in the Presence of Varying Amounts of TNT.

Preliminary analysis of the nature of the response shows that the observed effect is due to an exothermic reaction on the surfaces of the microcantilever in the presence of TNT. Further work is in progress to understand the mechanism by which the cantilever response is modified in the presence of TNT.

CONCLUSIONS

Feasibility of detecting explosives such as TNT through detecting their vapors with piezoresistive microcantilevers has been explored. Experiments clearly show that TNT vapors adsorb onto the microcantilever surface and modify the response of the piezoresistive cantilever to an applied voltage pulse that heats the cantilever. Further work is needed to map out regimes under which selectivity can be achieved in detecting TNT vapors and to establish the mechanisms of interaction and detection.

ACKNOWLEDGMENTS

REFERENCES

1. A. Fainberg, Science, **255**, 1531 (1992).
2. J. I. Steinfleid and J. Wormhoudt, Annu. Rev. Phys. Chem., **49**, 203 (1998).
3. E. Bender, A. Hogan, D. Leggett, G. Miskolczy and S. MacDonald, Journal of Forensic Sciences, **37**, 1673 (1992).
4. T. Thundat, E.A. Wachter, S. L. Sharp and R. J. Warmack, Appl. Phys. Lett., **66**, 1695 (1995).
5. T. Thundat, P. I. Oden and R. J. Warmack, Microscale Thermophys. Eng., **1**, 185 (1997).
6. T. Thundat, G. Y. Chen, R. J. Warmack, D. P. Allison, E. A. Wachter, Anal. Chem., **67**, 519 (1995).
7. Roberto Raiteri, Massimo Grattarola, Hans-Jürgen Butt, and Petr Skládal, Sensors and Actuators B, **79**, 115 (2001).
8. P. I. Oden, Sensors and Actuators B, **53**, 191 (1998).
9. Hai-Feng Ji, K. M. Hansen, Z. Hu, and T. Thundat, Sensors and Actuators B, **72**, 233 (2001).
10. A. Mehta, S. Cherian, D. L. Hedden, and T. Thundat, Appl. Phys. Lett., **78**, 1637 (2001).
11. U.S. Patent 5,595,942.